

Method of producing derivatives of the 1,1-dimethyl-octahydronaphthalene series

Publication number: GB896039
Publication date: 1962-05-09
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Classification:
- international: C07C45/67; C07C49/553; C07C45/00; C07C49/00;
- European: C07C45/67; C07C49/553; C07C175/00A5;
 C07C175/00A5C; C07C175/00A6; C07C175/00A7
Application number: GB19590024524 19590716
Priority number(s): GB19590024524 19590716

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Abstract of GB896039

1 - 1-Dimethyl-octahydronaphthalene derivatives of formula <FORM:0896039/IV (b)/1> in which the broken lines indicate that a single double bond is present in one of the four positions shown are prepared by cyclising a compound of formula <FORM:0896039/IV (b)/2> wherein R2, R3 and R4 are hydrogen atoms or alkyl groups and R1 is a hydroxy, alkyl or alkoxy group or R1 is hydrogen and the compound is in the form of a Schiff's base, is cyclised with phosphoric acid or boron trifluoride, or mixtures thereof, at a temperature between -30 DEG C. and +75 DEG C. or with sulphuric acid and/or formic acid at a temperature between -30 DEG C. and +10 DEG C. The starting materials are obtained by a Diels-alder reaction between myrcene and an appropriate dienophile compound. The final products are odoriferous and may be used in perfumes. In examples: (1) myrcene and methyl acrylate are heated in the presence of phenyl-b -naphthylamine to give a starting material wherein R1=OCH3 and R2 to R4=H, which is cyclised with sulphuric acid, phosphoric acid or boron trifluoride to give 1 : 1-dimethyl-7-carbomethoxy - octahydronaphthalene and the starting materials and cyclised products wherein R1=CH3, R2=H, R3 and R4=CH3; R1=OCH3, R2=H, R3 and R4=CH3; R1=OCH3, R2=CH3, R3 and R4=H; R1=OH, R2=CH3, R3 and R4=H are similarly prepared: (2) the Schiff base (with aniline) of the starting material wherein R1 to R4=H is dissolved in benzene and heated with phosphoric acid to give 1 : 1-dimethyl-7-formyl-octahydronaphthalene.

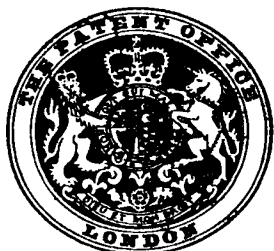
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PATENT SPECIFICATION

NO DRAWINGS

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896.039



Date of Application and filing Complete Specification: July 16, 1959.

No. 24524/59.

Complete Specification Published: May 9, 1962.

Index at acceptance:—Class 2(3), C3A5(C1B3:F2:H), C3A10(A4E:A4F:A5E:A5K:E3C1:E5E), C3A14A(2D:8A:8C).

International Classification:—C07c.

COMPLETE SPECIFICATION

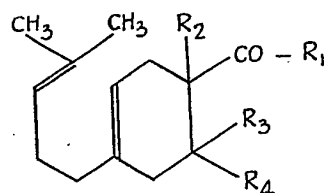
Method of producing Derivatives of the 1,1-Dimethyl-Octahydronaphthalene Series

We, DRAGOCO SPEZIALFABRIK KONZ. RIECH-U. AROMASTOFFE GERBERDING & CO. G.m.b.H., of Dragocostrasse, Holzminden/Weser, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of novel derivatives of 1,1-dimethyl-octahydronaphthalene with an oxygen-containing residue in the 7-position. Some of these hitherto unknown compounds excel by their outstanding suitability as perfumes because of their scent, fixability, and solubility in dilute alcohol, and they resemble the well known class of violet perfumes.

According to the invention, derivatives of the 1,1-dimethyl-octahydronaphthalene series are obtained by cyclisation of adducts of myrcene and dienophile compounds, obtained by Diels-Alder-synthesis, and having the

general formula



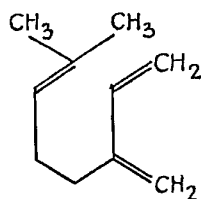
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wherein R_2 , R_3 and R_4 which may be the same or different are hydrogen atoms, or alkyl groups, and wherein R_1 is a hydroxy, alkyl, or alkoxy group, or in which R_1 is a hydrogen atom and the compound is in the form of a Schiff base, with phosphoric acid or boron trifluoride, or mixtures thereof, at temperatures between -30° and $+75^\circ$, or with sulphuric or formic acid, or mixtures thereof, at temperatures between -30° and $+10^\circ$.

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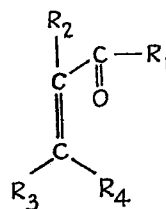
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The method of operation will be clear from the following reaction scheme:—

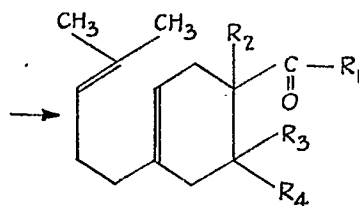


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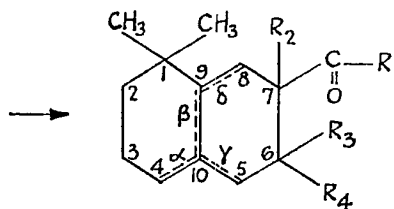
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II



III



IV

In Formula IV a double bond may be present in either the α -, β -, γ -, or δ -position as indicated by the broken lines.

The invention will now be illustrated by the following Examples:

EXAMPLE 1

1,1-Dimethyl-Octahydronaphthalene-7-Carboxylic Acid Methyl Ester.

1 mol myrcene was heated at 145 to 150°C. for two hours in an autoclave with 1½ mols acrylic acid methyl ester and with the addition of 0.5% of phenyl- β -naphthylamine. The yield of pure myrcene-acrylic acid methyl ester adduct of the general formula III, wherein $R_1 = \text{OCH}_3$ and R_2 to R_4 are hydrogen atoms, was 90% of theory. At a temperature of

Constants: —

$\text{bp}_{0.4} 105\text{--}107^\circ\text{C};$
ester content: —100%.

–15°, 300 g. of the hitherto unknown monocyclic ester (formula III; $R_1 = \text{OCH}_3$; R_2 to $R_4 = \text{H}$) were added dropwise, whilst the mixture was strongly agitated, to 2,000 c.c. of a 62% sulphuric acid, the addition being made in such manner that the temperature did not exceed +10°. About 45 minutes were spent in making the dropwise addition. Stirring of the mixture was continued at –7° for another hour, at the end of which further processing was in conventional manner. 255 g. (85% yield) of a 95% bicyclic ester could thus be obtained and the ester content could be increased to nearly 100% by fractional distillation.

The bicyclic ester appeared as a colourless, slightly viscous oil, principally consisting of the β -component. It had a weak violet and woody odour.

EXAMPLE 2.

1,1-Dimethyl-7-Carboxylic Acid Methyl Ester-Octalin.

300 g. ester of formula III ($R_1 = \text{OCH}_3$; R_2, R_3 and $R_4 = \text{H}$) were introduced as quickly as possible, whilst the mixture was being vigorously stirred, into 1000 g. of an 85% phosphoric acid, cooled to 0°C., in such manner that the temperature did not rise beyond +6°C. The reaction mixture was then rapidly heated to +55°C. and maintained at this temperature for 15 minutes. The contents of the reaction vessel were poured on to plenty of ice and extracted with ether. After neutralising the ethereal solution with water and boiling off the solvent, 290 g. (96% yield) of bicyclic ester with an ester content of 96.7% were obtained: —

Constants: —

$\text{bp}_{0.4} 118\text{--}120^\circ\text{C};$
ester content: —99.7%.

$d_{20}^{20} = 1.0100; \quad n_D^{20} = 1.4918;$

The bicyclic product (formula IV, $R_1 = \text{OCH}_3$; $R_2\text{--}R_4 = \text{H}$) had a delicate perfume similar to that of the bicyclic product obtained by treatment with sulphuric acid and consisted principally of an isomer with the double bond either in the α -, γ -, or δ -position.

EXAMPLE 3.

1,1-Dimethyl-7-Carboxylic Acid Methyl Ester-Octalin.

At a temperature of 0°C., whilst thoroughly stirring the mixture and excluding moisture, boron trifluoride was introduced into a solution of 224 g. of ester of formula III ($R_1 = \text{OCH}_3$; R_2, R_3 and $R_4 = \text{H}$) in 500 c.c. of absolute

toluene. As cyclisation proceeded the temperature rose. At +18° the reaction mixture was re-cooled to 0°C. and the remainder of the boron trifluoride was then added. The introduction of the whole of the necessary 70 g. of boron trifluoride was completed in ½ hour. For decomposing the boron trifluoride addition compound 600 c.c. of a 10% aqueous solution of caustic soda were added at a sufficiently slow rate to keep the temperature under +5°. The reacting solution separated into two layers. The aqueous solution was rejected, the solvent layer was washed with water until neutral, and the toluene was finally removed. The crude

bicyclic ester was distilled in a short column and yielded 204 g. of a product which in appearance was very similar to that obtained in Example 2.

Constants:—

5 $bp_{0.2}$ 110—112°C; $d^{20}_4 = 1.0150$; $n^{20}_D = 1.4941$
Ester content:—99.8%.

EXAMPLE 4

1,1-Dimethyl-7-Formyl-Octalin.

10 1 mol of an aldehyde of formula III (R_1 , R_2 , R_3 and $R_4 = H$), in the form of a Schiff base with aniline, was dissolved in an equal quantity of benzene and then added dropwise to 700 c.c. of an 85% phosphoric acid whilst the mixture was being vigorously stirred at 0°C. Stirring was continued for another hour at 60°C, in the course of which the cyclising reaction as well as the quantitative decomposition of the azomethine group were completed. The bicyclic aldehyde was now poured on to ice, taken up in benzene, and the solvent layer was washed with water until neutral. After the solvent had been distilled off, 190 g. of residue containing 82% aldehyde were obtained. The bicyclic crude aldehyde was then fractionated in a small column. 135 g. (= 70% of theoretical yield) of 1,1-dimethyl-7-formyl-octalin were thus obtained, consisting predominantly of an isomer with the double bond either in the α -, γ -, or δ -position.

Constants:—

30 $bp_{0.7}$ 96°C; $d^{20}_4 = 0.9884$; $n^{20}_D = 1.5042$;
aldehyde content:—98—100%.

EXAMPLE 5.

1,1,6,6-Tetramethyl-7-Ketomethyl-Octalin.

35 680 g. (5 mols) myrcene and 800 g. (8 mols) mesityl oxide were heated for 30 hours at 160°C. in an autoclave with the addition of 1 g. of phenyl- β -naphthylamine and 1 g. of

$bp_{0.6}$ 110—112°C; $d^{20}_4 = 0.9816$; $N^{20}_D = 1.4867$;

ester content:—93%.

EXAMPLE 7.

1,1-Dimethyl-7-Carboxylic Acid Methyl Ester-Octalin.

75 300 g. of an ester of formula III ($R_1 = OCH_3$; R_2 , R_3 and $R_4 = H$) were introduced as quickly as possible, and whilst the mixture was being vigorously stirred, into 1000 g. of an 85% phosphoric acid cooled to 0°C. in such manner that the temperature did not rise above

Constants:—

$bp_{0.4}$ 118—120°C; $d^{20}_4 = 1.0060$; $n^{20}_D = 1.4920$
ester content:—99.7%.

90 The bicyclic product (formula IV, $R_1 = OCH_3$; R_2 , R_3 and $R_4 = H$) evolved a similarly delicate perfume as the bicyclic product obtained by the sulphuric acid treatment and consisted principally of an isomer with the double bond either in α -, γ - or δ -position.

EXAMPLE 8.

1,1,7-Trimethyl- $\Delta^{8,10}$ - or (selectively) Δ^4 -Octahydronaphthalene-7-Carboxylic Methyl Ester.

pyrogallol. The yield of pure addition product of formula III, wherein $R_1 = CH_3$, $R_2 = H$, R_3 and $R_4 = CH_3$, was 111 g., i.e. 10% of the theoretical yield.

In the course of 1 hour 60 g. of the myrcene-mesityl oxide adduct were added dropwise to 500 c.c. of a 62% sulphuric acid which had been cooled to -10°C., the reaction mixture being then stirred for another hour. Processing was done in conventional manner. 53 g. of 1,1,6,6-tetramethyl-7-ketomethyl- $\Delta^{8,10}$ -octalin were thus obtained. The ketone appeared in the form of a viscous light yellow oil with a pleasant woody ambergris smell.

Constants:—

$bp_{1.5}$ 140—150°C; $d^{20}_4 = 0.949$; $n^{20}_D = 1.499$;
ketone content:—about 90%.

EXAMPLE 6.

1,1,6-Trimethyl-Octahydronaphthalene-7-Carboxylic Acid Methyl Ester.

80 g. of an ester of the general formula III ($R_1 = OCH_3$; R_2 and $R_3 = H$; $R_4 = CH_3$) were added dropwise at about +6° to 300 c.c. of a vigorously stirred 85% phosphoric acid. The reaction mixture was then heated to +75°C. and vigorous stirring was continued at this temperature for 30 minutes. The mixture was processed and 78 g. of the corresponding bicyclic ester of general formula IV were obtained, of which the following constants were determined:—

$bp_{0.6}$ 110—112°C; $d^{20}_4 = 0.9816$; $N^{20}_D = 1.4867$;

+6°C. The reaction mixture was then rapidly heated to +55°C. and maintained at this temperature for 15 minutes. The contents of the reaction vessel were poured on to plenty of ice and extracted with ether. After the ethereal solution had been washed with water until neutral and the solvent had been boiled off, 290 g. (96% yield) of bicyclic ester with a content of 96.7% were obtained.

612 g. (4.5 mol) myrcene and 500 g. (5 mol) α -methylacrylic acid methyl ester (formula II: $R_1 = OCH_3$; $R_2 = CH_3$; R_3 and $R_4 = H$) were heated for 3 hours to 145 to 150°C. in an autoclave, with the addition of about 1 g. phenyl- β -naphthylamine. Subsequent distillation through a distillation column yielded 650 g. (61% yield) of pure ester of formula III ($R_1 = OCH_3$; $R_2 = CH_3$; R_3 and $R_4 = H$).

500 g. of the resulting monocyclic ester were dissolved in 500 cc. of ethyl ether and added so slowly into 3500 cc. of 62% sulphuric acid, with vigorous stirring, that the temperature never rose above 0°C. The mixture was then stirred for a further hour at -5°C., and then poured onto a large quantity of ice, and taken up with benzene during which the ice slowly melted. The resulting aqueous lower layer was separated by decanting and was extracted three times with benzene until it was free from

reaction product. The benzene layer and the benzene used for the extraction were combined and washed until the washings were neutral whereupon the solvent was evaporated. The residue was the dicyclic ester which was purified by vacuum distillation and which consisted mainly of 1:1:7-trimethyl- $\Delta^{9,10}$ -octahydronaphthalene-7-carboxylic methyl ester (formula IV; R = OCH₃; R₂ = CH₃; R₃ and R₄ = H). The ester was thereby produced in 65% yield.

Constants:—

bp_{2.3} 128—130°C; D₂₀⁴ = 1.0094; n_D²⁰ = 1.4882;
ester content 100%.

If the cyclisation of the Diels-Alder adduct is carried out with boron trifluoride instead of with sulphuric acid, in accordance with the method used in Example 3, the yield of 1:1:7-trimethyl-octahydronaphthalene-7-carboxylic-acid-methyl-ester may be raised from 61 to 93.8%.

Whereas the cyclisation product obtained with acid catalysis consists mainly of the $\Delta^{9,10}$ -octalin derivative, when the cyclisation is carried out with boron trifluoride, the double bond is mainly directed to the Δ^4 -position.

EXAMPLE 9.

1.1.7-Trimethyl- $\Delta^{9,10}$ - or (selectively) Δ^4 -Octahydronaphthalene-7-Carboxylic Acid.

9a). 612 g. (4.5 mol) myrcene and 430 g. (5 mol) α -methylacrylic acid were heated with the addition of 1 g. of phenyl- β -naphthylamine for 3 hours to 150°C. in an autoclave. Subsequent distillation through a column yielded 670 g. (67% of the theoretical yield) of pure adduct acid.

(formula III; R₁ = OH; R₂ = CH₃; R₃ and R₄ = H).

Boron trifluoride was introduced at 0°C. and with vigorous stirring and exclusion of moisture into a solution of 500 g. of the myrcene- α -methacrylic acid-adduct in 1000 cc. of absolute toluene. With progressive ring closure, the temperature rose. At +18°C. the reaction mixture was treated with the remainder of the boron trifluoride until 140 g. of boron trifluoride had been added, the addition taking 45 minutes. In order to decompose the boron trifluoride complex, the reaction mixture was then treated so slowly with 1200 cc. of a 10% aqueous sodium hydroxide solution that the temperature did not rise above 5°C. The reaction solution separated into 2 layers. The solvent layer was removed and the aqueous solution was treated with concentrated sulphuric acid until neutral. The cyclisation product separated completely. Yield: 460 g. (92% of theoretical).

The major portion of the cyclisation product crystallised and consisted of 1:1:7-trimethyl- Δ^4 -octahydronaphthalene-7-carboxylic acid. (formula IV; R₁ = OH; R₂ = CH₃; R₃ and R₄ = H).

M.p. 69°C. (from acetonitrile); S-benzylthiouronium salt; M.p. 128° (from dilute methanol).

9b). The Diels-Alder adduct obtained from myrcene and α -methacrylic-acid-ester may be converted before cyclisation into the corresponding adduct acid, if the ester is boiled with more than the stoichiometric quantity of a 10 percent alcoholic potassium hydroxide solution.

The liquid acid may then be converted into the cyclisation product in the same manner as just described above under 9a).

9c). In order to prepare selectively the Δ^4 - and $\Delta^{9,10}$ -1:1:7-trimethyl-octahydronaphthalene-7-carboxylic acids the two esters obtained by the process described in Example 8 may be saponified by the process just described under 9b).

Constants:—

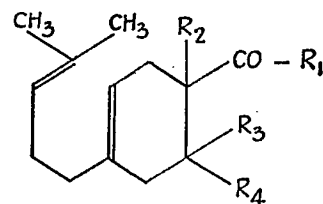
1:1:7-trimethyl- Δ^4 -octahydronaphthalene-7-carboxylic acid: M.p. 69°.

1:1:7-trimethyl- $\Delta^{9,10}$ -octahydronaphthalene-7-carboxylic acid: M.p. 63°.

The novel compounds obtained by the method according to the invention are valuable perfumes distinguished from known compounds by their new and distinctive scents and from other octahydronaphthalene derivatives by their outstanding clinging properties.

WHAT WE CLAIM IS:—

1). A method of producing derivatives of the 1,1-dimethyl-octahydronaphthalene series, wherein a compound of the general formula:



in which R₂, R₃, R₄ which may be the same or different are hydrogen atoms, or alkyl groups, and in which R₁ is a hydroxy, alkyl, or alkoxy group, or in which R₁ is a hydrogen

5 atom and the compound is in the form of a Schiff base, is cyclised with phosphoric acid or boron trifluoride, or mixtures thereof, at a temperature between -30°C. and $+75^{\circ}\text{C.}$, or is cyclised with sulphuric acid or formic acid, or mixtures thereof, at a temperature between -30°C. and $+10^{\circ}\text{C.}$

2). A method as claimed in Claim 1, wherein R_1 is a methoxy group.

3). A method of producing derivatives of the 1,1-dimethyl-octahydronaphthalene series substantially as hereinbefore described in any one of the foregoing Examples. 10

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1962.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.